

INFLUENCE OF AIRFIELD PAVEMENT DEICING AND ANTI-ICING CHEMICALS
ON DURABILITY OF CONCRETE

By:
Prasada Rao Rangaraju
Assistant Professor
Department of Civil Engineering
Clemson University
Clemson, SC, 29634-0911
USA
Phone: (864) 656-1241 ; FAX (864) 656-2670
prangar@clemson.edu

PRESENTED FOR THE
2007 FAA WORLDWIDE AIRPORT TECHNOLOGY TRANSFER CONFERENCE
Atlantic City, New Jersey, USA

April 2007

ABSTRACT

Following observations of premature deterioration in some airfield concrete pavements exposed to deicing and anti-icing chemicals, a comprehensive laboratory-based research study was undertaken to investigate the effect of these chemicals on concrete. In particular, the potential of these chemicals to induce alkali-silica reaction (ASR) distress in mortar and concrete test specimens was investigated. The deicing chemicals evaluated in this study include potassium acetate, sodium acetate and sodium formate-based formulations. In this study, mortar and concrete test specimens prepared with aggregates of known reactivity (both reactive and non-reactive in nature) were exposed to deicer solutions for a defined period of time. The distress in the test specimens was periodically documented and characterized. The characterization studies included measuring changes in length, modulus of elasticity and microstructure of test specimens. In addition, the pH of the solution in which test specimens were immersed was also monitored. Based on the results it was ascertained that the principal distress observed in the test specimens exposed to all of the three deicing chemicals was due to alkali-silica reaction (ASR). However, presence of certain secondary reaction products in test specimens exposed to potassium acetate deicer was observed. The effect of these secondary products on the durability of concrete needs to be further investigated.

INTRODUCTION

Chemical deicing and anti-icing agents are routinely used for ice and snow removal operations in many airports across the world. In past, chemicals such as urea, ethylene glycol (EG), propylene glycol (PG), and blends of PG and urea have been successfully used on airfield pavements as deicing and anti-icing agents. However, environmental concerns arising from high biological oxygen demands of glycols and urea in runoff streams, and concerns with the toxicity of these chemicals to aquatic life have lead to regulations on such uses of glycols and urea [1, 2]. In response to these limitations a new generation of deicers had emerged in early 1990s that were based on alkali-acetate and alkali-formate formulations. Since then deicers and anti-icers such as potassium acetate (KAc), sodium acetate (NaAc), potassium formate (KFr) and sodium formate (NaFr) have seen an enormous growth in their use as anti-icing and deicing agents on airfield pavements.

Coincidentally, in last 15 years an increased number of airfield pavements have reported premature deterioration in airfield concrete pavements. Recent investigations into deterioration of several commercial concrete airfield pavements indicated Alkali-Silica Reaction (ASR) to be one of the principal reasons for deterioration. These airfields included: Colorado Springs Airport (COS), Denver International Airport (DEN), Salt Lake City International Airport (SLC), Detroit Metropolitan International Airport (DTW), Hartsfield-Jackson Atlanta International Airport (ATL), Greenville-Spartanburg International Airport (GSP), Memphis International Airport (MEM) and others. In some of these airports including COS, DIA, SLC and DTW, it has been suspected that the exposure of the concrete pavement to the alkali-acetate and alkali-formate deicers may have played a role in either triggering or accelerating ASR distress. Figure 1 shows typical distress observed in airfield concrete pavements exposed to deicing chemicals.



Figure 1. Distress in Concrete Pavement Exposed to Deicers at Colorado Springs Airport, CO, U.S.A

ASR DISTRESS AND FACTORS

ASR is a chemical reaction that occurs when alkali hydroxides present in the pore solution of the concrete react with certain forms of amorphous and poorly crystalline silica. The reaction produces a hygroscopic ASR gel that expands upon absorbing moisture, creating tensile stresses within concrete. This process eventually leads to extensive cracking within the concrete. Typically, alkali hydroxides such as sodium hydroxide and potassium hydroxide are derived from soluble alkali-sulfates normally present in the portland cement clinker. Other sources of alkali that may contribute to the alkali hydroxide loading of the concrete include supplementary cementing materials, chemical admixtures, mix water, and/or certain aggregates [3-6]. The aforementioned sources of alkalis are internal to concrete matrix. In certain situations the alkali loading in concrete may come through ingress of alkalis from external environments, such as alkali-based deicers, sea water spray and brackish ground waters, thus potentially leading to conditions ideal for occurrence of ASR.

Considerable research has been conducted in past on studying the influence of external sources of alkali from deicing salts such as sodium chloride on initiating or aggravating ASR [7-11]. However, the influence of the new generation of deicers, such as the alkali-acetate and alkali-formate based deicers, on the potential to cause or accelerate ASR in concrete has not yet been studied.

EXPERIMENTAL APPROACH AND SCOPE

In order to investigate the potential of these chemicals to cause ASR distress in concrete, a comprehensive laboratory-based research study was undertaken. The test methods employed in this research are based on standard and modified versions of ASTM C 1260 and ASTM C 1293 test methods. In this study, mortar and concrete test specimens prepared with six different

aggregates of different mineralogy and reactivity were exposed to solutions of either 1 normal sodium hydroxide (1N NaOH) or commercial deicing and anti-icing chemicals for a defined period of time. During the course of the exposure, the test specimens were periodically characterized for changes in length, modulus of elasticity and microstructure. In addition, the pH of the solution in which test specimens were immersed was also monitored.

The deicing chemicals evaluated in this study include potassium acetate, sodium acetate, sodium formate and potassium formate-based formulations. Concrete prisms and mortar bar test specimens were prepared with 4 reactive aggregates and 2 non-reactive aggregates in combination with two ASTM C 150 Type I portland cements that differed significantly in their alkali content. Finally, selected studies were conducted to investigate the influence of concentration of deicer solutions and temperature of the test method on the severity of the observed distress. For each test four test specimens were cast to obtain an average result from four observations. In this study over 400 test specimens were cast and tested. In order to provide a representative yet concise summary of this research study, the results obtained from tests conducted using only one reactive aggregate and one non-reactive aggregate in combination with three of the major deicing and anti-icing chemicals used in the United States (KAc, NaAc and NaFr) and 1N NaOH solution will be presented.

EXPERIMENTAL PROGRAM

Materials

Chemicals

In this study, a commercial grade liquid KAc deicer/anti-icing formulation with a concentration of 50% by weight was used as soak solution in the modified ASTM C 1260 and ASTM C 1293 tests. The pH of the commercial KAc deicer solution was 10.85. NaAc and NaFr deicers are commercially sold as solid pellets. In this study saturated solutions of NaAc and NaFr at room temperature were used as soak solutions, as this concentration represented a possible worst case scenario from an exposure standpoint. A reagent grade sodium hydroxide was used at a 1 normal concentration in the standard and modified ASTM C 1293 tests.

Aggregates

The non-reactive coarse aggregate used in this study was a quarried dolomite from Illinois, U.S.A. This aggregate has an established history of good field performance and has been used as a reference non-reactive aggregate in ASTM C 1293 tests in other laboratory studies [12]. This aggregate is represented as “IL” in the results section. The non-reactive fine aggregate used in this study was the standard Ottawa sand from Illinois, U.S.A. Although four reactive coarse aggregates were used in this study, for sake of brevity and considering the limits on the length of the paper, results from one typical reactive aggregate – Spratt limestone – are presented in this paper. Spratt limestone was obtained from Spratt quarry in Ontario Province of Canada. It primarily consists of calcite with minor amounts of dolomite and about 10% of insoluble residue. The reactive component of the rock is reported to consist of 3% to 4% of microscopic chalcedony and black chert, which is finely dispersed in the matrix [13]. This aggregate has an established history of being alkali-silica reactive in field structures and has been used as a reference aggregate in numerous ASR studies. This aggregate is identified in the results as “Spratt”. Table 1 gives the properties of the aggregates used in this study.

Table 1. Properties of Coarse and Fine Aggregates

Aggregate Property	Coarse Aggregates		Fine Aggregate
	Spratt, Limestone (Reactive)	IL, Dolomite (Non-reactive)	IL, Ottawa Sand
Water absorption, %	0.456	2.12	0.05
Bulk specific gravity (Oven-Dry)	2.69	2.66	2.65
Bulk specific gravity (Saturated Surface Dry)	2.70	2.71	2.65
Dry-Rodded Unit Wt., kg/m ³	1568	1563.7	---

Cement

In this study two different ASTM C 150 Type I portland cements were used – a high-alkali cement and a low-alkali cement. The oxide composition of the cements is reported in Table 2.

Table 2. Chemical Composition of Cements Used in Preparing Test Specimens

Oxide	High-Alkali Cement (%) (HA)	Low-Alkali Cement (%) (LA)
SiO ₂	19.74	20.3
Al ₂ O ₃	4.98	5.0
Fe ₂ O ₃	3.13	3.4
CaO	61.84	64.45
MgO	2.54	1.2
SO ₃	4.15	2.8
LOI	1.90	1.85
Na ₂ O _{equivalent}	0.82	0.31
K ₂ O	0.84	0.36
Na ₂ O	0.27	.07
Insoluble Residue	0.25	0.17
Clinker Compounds*	Potential Composition Based on Bogue's Calculation	
C ₃ A	8.97	7.20
C ₃ S	46.6	63.76
Autoclave Expansion (%)	0.12	0.08

* The clinker compound percent listed in Table 2 is based on the information supplied by the cement manufacturer.

Mortar and Concrete Proportions

Mortars for the test specimens in the standard and modified ASTM C 1260 tests were prepared using 2.25 parts of fine aggregate with 1 part of cement at a water-to-cement ratio of 0.47. The fine aggregate used in the mortars was prepared from crushing the coarse aggregates and sieving

and washing to meet the gradation requirements specified in the standard ASTM C 1260 test method. The proportions of materials used in preparing the concrete prisms for the standard and modified ASTM C 1293 tests and the properties of fresh concrete are given in Table 3.

Table 3. Concrete Mixture Proportions Used in Preparation of Concrete Prisms for the Standard and Modified ASTM C 1293 Tests (per cubic meter).

Materials	Coarse Aggregate Type	
	Spratt (Reactive)	IL Dolomite (Non-reactive)
Cement, kg/m ³	420	420
Fine agg, kg /m ³	678	669
Coarse agg, kg/ m ³	1102	1117
Water, kg/ m ³	182.7	182.7
W/C	0.435	0.435
Agg/Cem	4.24	4.25
Density, kg/m ³	2383	2389
Actual density, kg/m ³	2401	2410
Actual cement, kg/m ³	423	423
Slump, mm	65	50

Note: 2.33 kg/m³ of reagent grade sodium hydroxide was added to the mix water in concrete prepared with high-alkali cement as per the standard ASTM C 1293 requirement. This resulted in a total alkali content of 1.25% Na₂O by mass of cement in the concrete mixture.

Test Methods

Standard and Modified ASTM C 1260 Test Methods (Mortar Bars)

In this test method, mortar bars (25 mm x 25 mm x 285 mm) with embedded gage studs are cast and cured for 24 hours in a moist curing room. After demolding, the bars are cured for an additional 24 hours in a water bath that is gradually heated from ambient temperature to 80°C. At the end of water-bath curing, the bars are transferred to an 80°C bath of either 1 N NaOH solution (standard ASTM C 1260 test) or a specific deicer or anti-icer solution under consideration (modified ASTM C 1260 test). Previous investigation on the effect of soak solution temperature on expansion of mortar bars has shown that higher temperatures merely accelerate the reaction mechanism (in both 1N NaOH and deicer solution) compared to mortar bars tested at lower temperature and do not result in any unanticipated deviations in mechanisms [14]. Periodic length-change measurements are taken over the course of the following 28 days and the percent expansion is calculated. Based on the guidance provided in ASTM C 33 for the standard ASTM C 1260 test expansions less than 0.1% at 14 days in the standard ASTM C 1260 test are typically considered to represent non-reactive aggregates. Expansions over 0.2% at 14 days are considered to represent potentially reactive aggregates. Expansion values between 0.1% and 0.2% require additional confirmation by concrete prism test (ASTM C 1293 test) or from past field performance. Similar limits were considered in interpreting the data resulting from the modified ASTM C 1260 tests.

Standard and Modified ASTM C 1293 Test (Concrete Prism Test)

In the standard ASTM C 1293 test method, concrete prisms (75 mm x 75 mm x 285 mm) are prepared with the aggregate in question (coarse or fine aggregate) along with a non-reactive supplementary aggregate (fine or coarse aggregate). The cement to be used in this test is required to have a minimum alkali content of $0.9\% \pm 0.1\% \text{ Na}_2\text{O}_{\text{eq}}$. With the addition of sodium hydroxide to the mix water, the alkali content of the concrete mix is then raised to $1.25\% \text{ Na}_2\text{O}_{\text{eq}}$ by mass of cement in the mix. The concrete prisms are then stored in sealed containers that maintain a 100% relative humidity. The sealed containers are then placed in a 38°C environment. Periodic length change measurements are taken up to one year. A level of expansion greater than 0.04% at one year is indicative of the reactive nature of the aggregate.

The intent of the modified ASTM C 1293 test is to determine the potential of the deicing solution to cause ASR in concrete test specimens. In the modified ASTM C 1293 test method, the concrete prisms are prepared in a manner similar to the standard test method. However, instead of storing the prisms in a 100% relative humidity environment at 38°C , the prisms were soaked in deicer solution at 38°C . For tests with KAc deicer, the concrete prisms were soaked in a 50% wt. solution of KAc deicer, and for tests with NaAc and NaFr deicers saturated solutions of respective deicers at room temperature were used. While the concentration of the deicer solutions is relatively high, it should be noted that these concentrations represent the field application and/or worst possible scenario anticipated during deicing and anti-icing operations. Parallel tests were conducted in which concrete prisms were soaked in 1N NaOH solution, to serve as a “control” in the modified ASTM C 1293 tests.

When using the high-alkali cement in preparing the concrete prisms for the modified ASTM C 1293 test method, the alkali content of the concrete was raised to $1.25\% \text{ Na}_2\text{O}_{\text{eq}}$ by mass of cement by adding reagent grade NaOH as per the standard ASTM C 1293 standard procedure. However, when low-alkali cement was used no additional NaOH was added to the mix water. This modification produced a set of prisms, where the only significant source of alkali to trigger ASR came from the external soak solution. This comparative study enabled the assessment of influence of deicer solutions on ASR.

Dynamic Modulus of Elasticity

The physical distress in concrete prisms was quantified by measuring their dynamic modulus of elasticity (DME). The DME values were determined using the resonant frequency method based on impulse excitation technique (ASTM E 1876-01). A GrindoSonic™ instrument was used in determining the resonant frequencies of the concrete prisms. The mass and the resonant frequency of the concrete prisms were measured soon after the prisms were removed from the soak solution for expansion measurements. For sake of simplicity, the dimensions of the concrete prisms were assumed to be constant (i.e., 75 mm x 75 mm x 285 mm) and the effects of gage studs at the ends of the prisms were neglected as it was a common factor for all measurements and would have a relatively small effect on the dynamic modulus of elasticity results.

pH of Soak Solution

In order to track any changes in the hydroxyl ion concentration of the soak solution, its pH was monitored. The pH measurements were made soon after the length-change measurements were made on the concrete prisms. The pH of the soak solution was determined by using an Oakton

pH meter with an Accumet low-sodium error pH probe. Before every reading, the probe was calibrated using buffer solutions with a pH of 4, 7, 10 and 12.45.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) Analysis

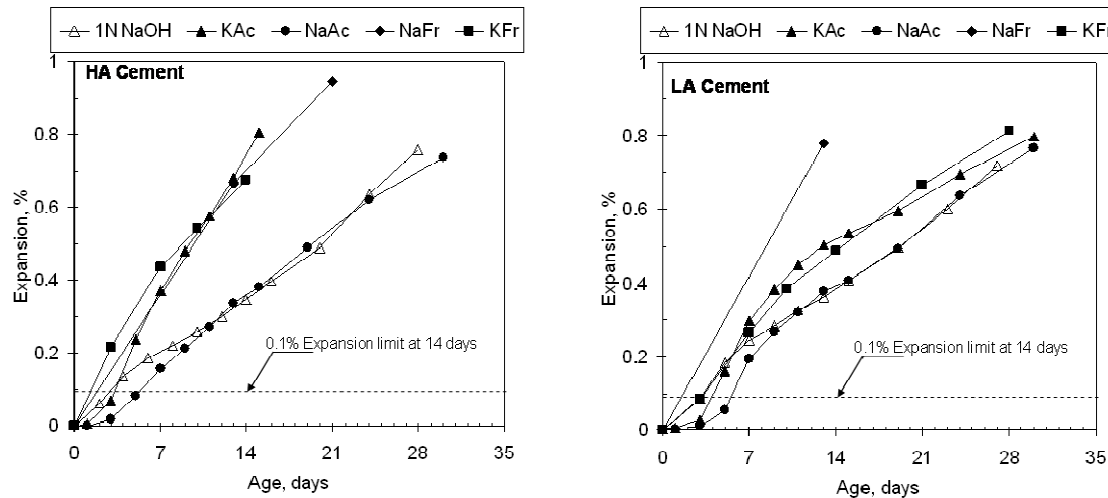
SEM in back-scattered mode and EDX analysis were conducted on polished sections of concrete prisms from the standard and modified ASTM C 1293 tests, using a Hitachi S3400N electron microscope. The instrument was operated in a variable pressure mode at a 30Pa vacuum and an accelerating voltage of 20KeV. The EDX was calibrated using Copper $K\alpha$ peak.

The samples for the SEM investigation were prepared by slicing the prisms using a slow speed diamond saw followed by polishing the samples on a series of magnetic lapping wheels with embedded diamond grit. The final polishing step involved the use of a 0.5 micron diamond paste on a cloth lap.

RESULTS AND ANALYSIS

Results of Standard and Modified ASTM C 1260 Tests

Figures 1a and 1b show the expansion behavior of mortar bars prepared with Spratt limestone high-alkali cement and low-alkali cement, respectively.



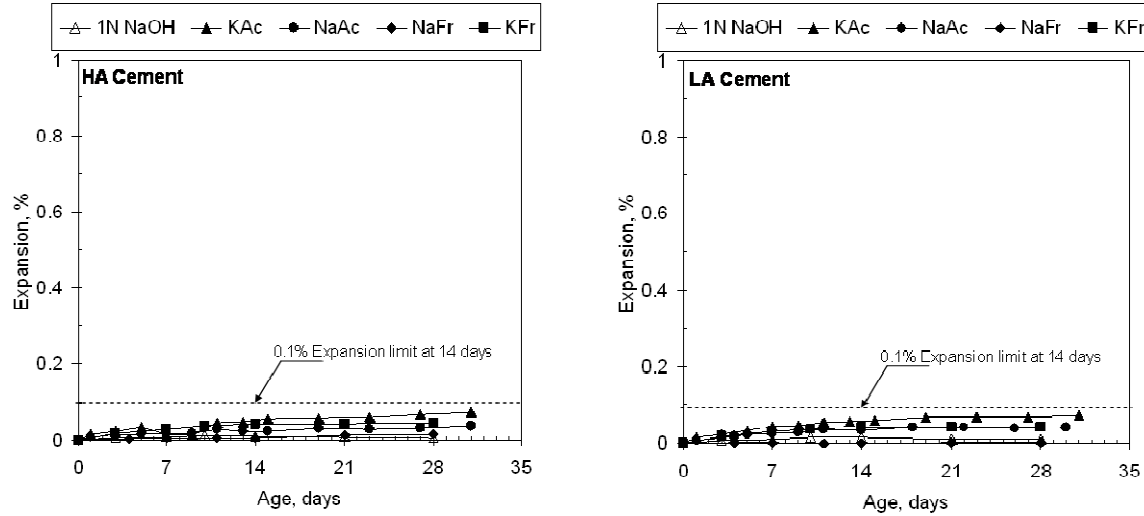
(a) Spratt – High-Alkali Cement Mortar Bars

(b) Spratt – Low-Alkali Cement Mortar Bars

Figure 1. Expansion of Spratt limestone mortar bars (prepared with HA and LA cements) exposed to different soak solutions in the standard and modified ASTM C 1260 tests.

From these results it is apparent that regardless of the alkali content of the cement used in the Spratt limestone mortar bars, all the deicer soak solutions (KAc, NaAc, NaFr and KFr) and 1 N NaOH solution caused significant expansion (i.e. > 0.1% at 14 days). This suggests that the deicing solutions are capable of inducing severe ASR distress in test specimens containing reactive aggregates.

Figures 2a and 2b show the expansion behavior of mortar bars prepared with the non-reactive Ottawa sand.



(a) Ottawa – High Alkali Cement Mortar Bars

(b) Ottawa – Low Alkali Mortar Cement Bars

Figure 2. Expansion of Ottawa sand mortar bars (prepared with HA and LA cements) exposed to different soak solutions in the standard and modified ASTM C 1260 tests.

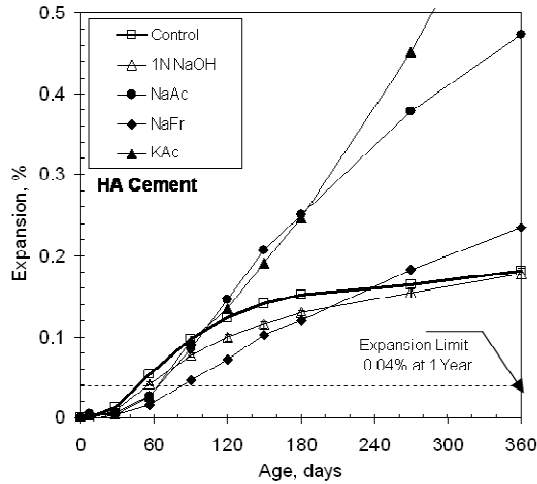
It is evident from the results that regardless of the alkali content of the cement, none of the soak solutions were capable of inducing expansion greater than 0.1% expansion at 14 days in mortar bars containing non-reactive aggregate. The data presented in Figures 2a and 2b show that even at later ages (i.e. up to 28 days) no expansion significant increase in expansion could be observed. However, it should be pointed that mortar bars soaked in KAc, KFr and NaAc deicer solutions showed slightly more expansion than mortar bars soaked in 1N NaOH solution and NaFr solution. It is likely that the Ottawa sand, typically considered as non-reactive based on tests with 1N NaOH solution, may have been attacked by the deicer solutions.

Results of Standard and Modified ASTM C 1293 Tests

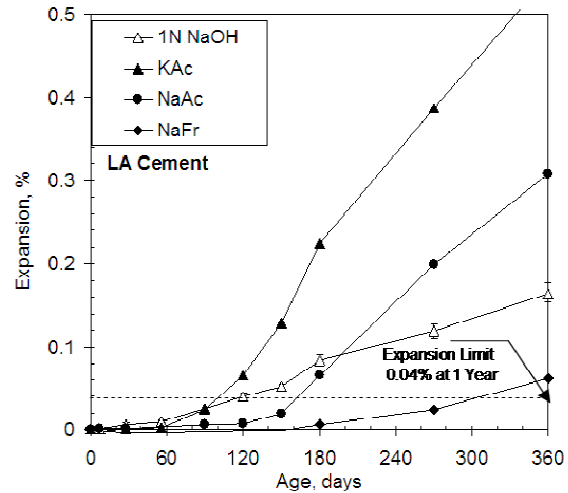
Figures 3 and 4 show the results from the standard and modified ASTM C 1293 tests conducted on concrete prisms prepared with the reactive Spratt limestone aggregate and non-reactive IL dolomite aggregates, respectively. The influence of cement alkalinity on the expansions observed in the concrete prisms is shown in Figures 3a and 3b for Spratt limestone aggregate and Figures 4a and 4b for IL dolomite aggregate.

The standard ASTM C 1293 test method calls for a cement with an alkali content of $0.9 \pm 0.1\%$ Na_2O content. Therefore, control tests (i.e. standard ASTM C 1293 tests) were conducted only on test specimens using HA cement. No control test specimens were cast for the LA cement series of tests.

In the modified ASTM C 1293 test the concrete prisms prepared with both HA and LA cement were exposed to different deicer solutions including KAc, NaAc and NaFr and 1N NaOH solution. KFr was not evaluated in this study.

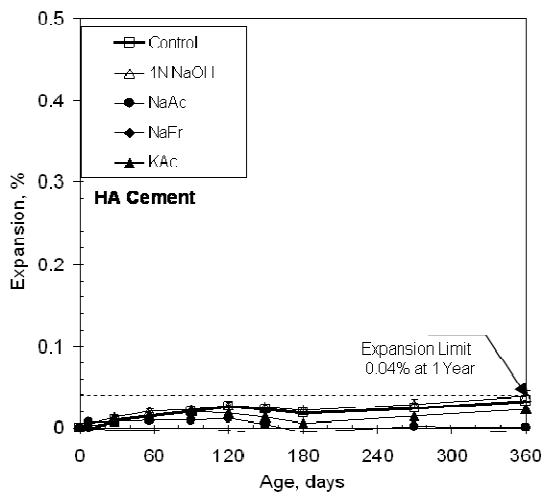


(a) Spratt – High-Alkali Cement Prisms

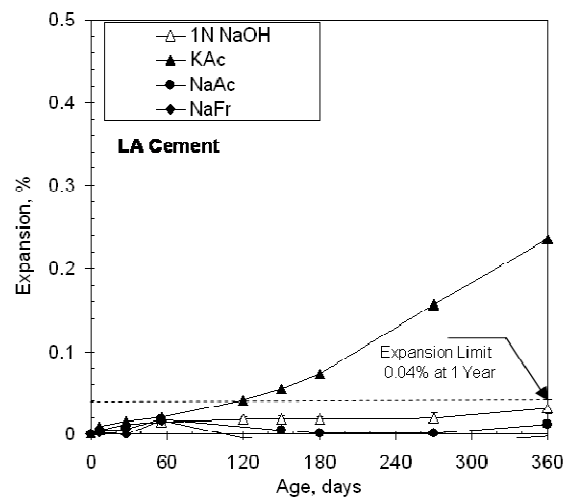


(b) Spratt – Low-Alkali Cement Prisms

Figure 3. Expansion of Spratt limestone concrete prisms (with HA and LA cements) exposed to different soak solutions in the standard and modified ASTM C 1293 tests.



(a) IL Dolomite–High-Alkali Cement Prisms



(b) IL Dolomite – Low-Alkali Cement Prisms

Figure 4. Expansion of IL dolomite concrete prisms (with HA and LA cements) exposed to different soak solutions in the standard and modified ASTM C 1293 tests.

Results from Figure 3 shows that all the deicer solutions caused significant expansion in the concrete prisms at one year (i.e. $> 0.04\%$ at one year). However, the alkali content of the cement used in preparing the concrete prisms and the type of the soak solution employed appear to have a distinct effect on the rate of expansion observed in these tests. The prisms prepared with high-alkali cement showed significant expansion in the standard ASTM C 1293 test and the modified ASTM C 1293 tests from early ages, regardless of the type of the soak solution. In contrast, prisms prepared with low-alkali cement showed a slower rate of expansion in the modified ASTM C 1293 tests with all the deicer and 1N NaOH soak solutions at early ages. However, at later age significant increase in rate of expansions were observed in the low-alkali prisms

depending on the type of the soak solution employed. This suggests the distinct influence of external alkali source in triggering deleterious reactions in the test specimens.

Among the different soak solutions evaluated with the low-alkali concrete prisms, KAc deicer solution and 1N NaOH solution caused the most expansion at early ages (i.e. < 120 days). At later ages KAc and NaAc deicer solutions caused the most expansion, followed by 1N NaOH solution. NaFr deicer solution caused the least expansion in the low-alkali concrete prisms among all the soak solutions. However, at one year exposure period, even NaFr deicer solution caused sufficient expansion in the prisms (> 0.04%) to be deemed deleterious.

Results from Figure 4a show that the non-reactive IL dolomite did not show any significant expansion at one year of age, in the standard and modified ASTM C 1293 tests when high-alkali cement was used in the test specimens. Figure 4b shows the response of the low-alkali concrete prisms to different soak solutions in the modified ASTM C 1293 tests. While 1N NaOH solution and NaAc and NaFr deicer solutions did not cause any significant expansion in the low-alkali concrete prisms, KAc deicer solution caused significant expansion as early as 120 days. While this behavior was not anticipated, microstructural examination of test specimens showed mechanisms other than ASR affecting the concrete prisms that had resulted in the expansion. These findings will be presented in the section on microstructural study.

Dynamic Modulus of Elasticity (DME)

Concrete prisms subjected to standard and modified ASTM C 1293 tests were evaluated for their dynamic modulus of elasticity, in order to assess the progressive deterioration in the structural integrity of the prisms.

Figure 5 shows the percent change in DME of Spratt limestone and IL dolomite concrete prisms subjected to the standard and modified ASTM C 1293 tests relative to their initial DME (taken as 100%). It can be observed from Figure 5 that in all the standard and modified ASTM C 1293 tests involving Spratt limestone, there is an initial increase in the DME value up to 60 days, followed by a gradual drop in DME to values less than 100% at 360 days. It appears that the continued hydration of cement and the associated gain in strength and stiffness caused the initial increase in DME values. However, at later ages the distress caused by ASR resulted in significant loss of DME. The observed loss was greatest for prisms soaked in KAc deicer solution compared to other deicer solutions, 1N NaOH solution and 100% relative humidity environment. In all the cases, DME dropped below 100% suggesting the onset of active ASR-related deterioration in test specimens.

In case of concrete prisms with IL dolomite in the standard and modified ASTM C 1260 tests, there is an initial increase in the DME values of the prisms up to 120 days, followed by a drop at later ages. However, in all the cases the DME of IL dolomite concrete prisms at one year is near or above 100% suggesting no severe structural deterioration in the concrete prisms. The reason for the drop in DME values of IL dolomite prisms at later ages, regardless of the storage condition, is not entirely evident at this point of time and needs further investigation. Unlike Spratt limestone concrete prisms, IL dolomite concrete prisms did not exhibit any visible cracks on the surface of the specimens.

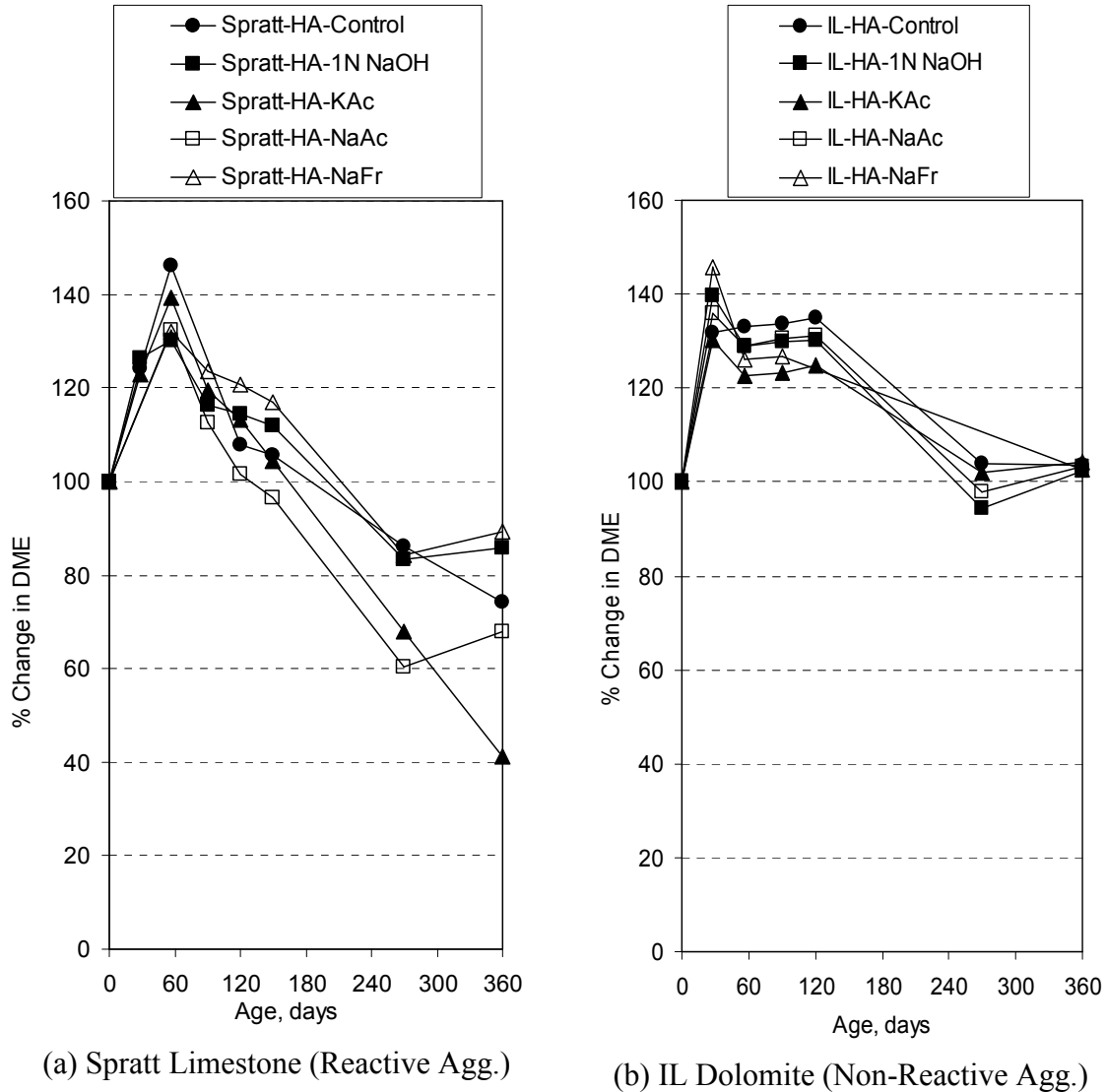


Figure 5. Percent Change in DME of Concrete Prisms Subjected to Standard and Modified ASTM C 1293 Tests

pH of Soak Solution

pH of the soak solutions was monitored to study the interaction of the soak solutions with the concrete prisms. Figure 6 shows the representative pH data of the soak solutions from the modified ASTM C 1293 tests with Spratt limestone and IL dolomite. In particular, the pH of soak solution before immersing the concrete prisms and after one year of soaking the prisms in the solution is presented. The pH of the soak solution before immersing the prisms is identified in the graph as “plain”, and the pH of the soak solution in which concrete prisms prepared with Spratt limestone and IL dolomite were soaked are identified as “Spratt” and “IL”, respectively. It should be noted that the pH of the soak solutions was measured at 38°C – the storage temperature during the course of the tests.

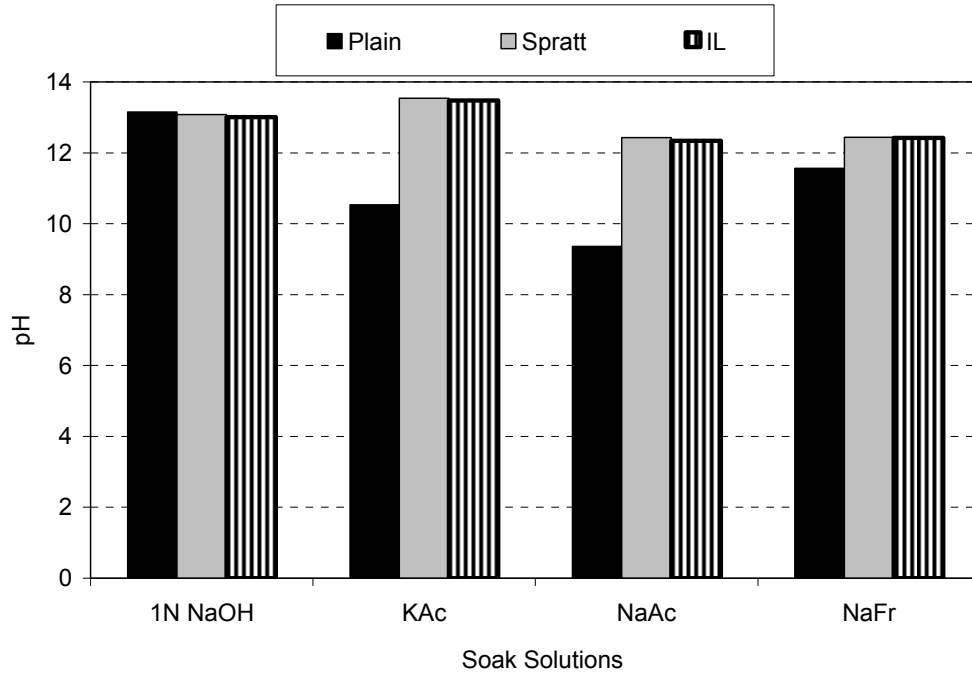


Figure 6. pH of soak solution before and after soaking the concrete prisms in the modified ASTM C 1293 test on Spratt limestone and IL dolomite.

It can be observed from the data shown in Figure 6 that in case of Spratt limestone and IL dolomite the pH of the 1N NaOH solution was identical before and after soaking the concrete prisms. However, in case of KAc and NaAc deicer soak solutions, a significant jump in the pH of the soak solutions was observed between plain solution and solutions in which concrete prisms prepared with Spratt limestone and IL dolomite were stored. Similar change in pH, but to a lesser extent, was observed in the case of NaFr deicer solution.

In a separate investigation by the authors it was found that the “pH jump” phenomenon observed in KAc, NaAc and NaFr deicer solutions was caused by an interaction between the deicer solutions and calcium hydroxide in the hydrated cement paste [14, 15]. It is suspected that the high pH resulting from the interaction between deicer solutions and the calcium hydroxide is triggering deleterious ASR reaction in case of concrete prisms containing reactive aggregates such as Spratt limestone. The consequence of the increase in pH of deicer soak solutions on concrete prisms containing non-reactive IL dolomite aggregate is not clear at this time. Although no deleterious ASR reaction was observed in these prisms, a notable drop in the dynamic modulus of elasticity was observed. Further studies to address these findings are being conducted.

Micro-structural Observations

Figure 7 shows the back-scatter SEM images from polished sections of Spratt limestone concrete prisms with HA cement in the standard ASTM C 1293 test and in the modified test where the prisms are soaked in 1N NaOH solution.

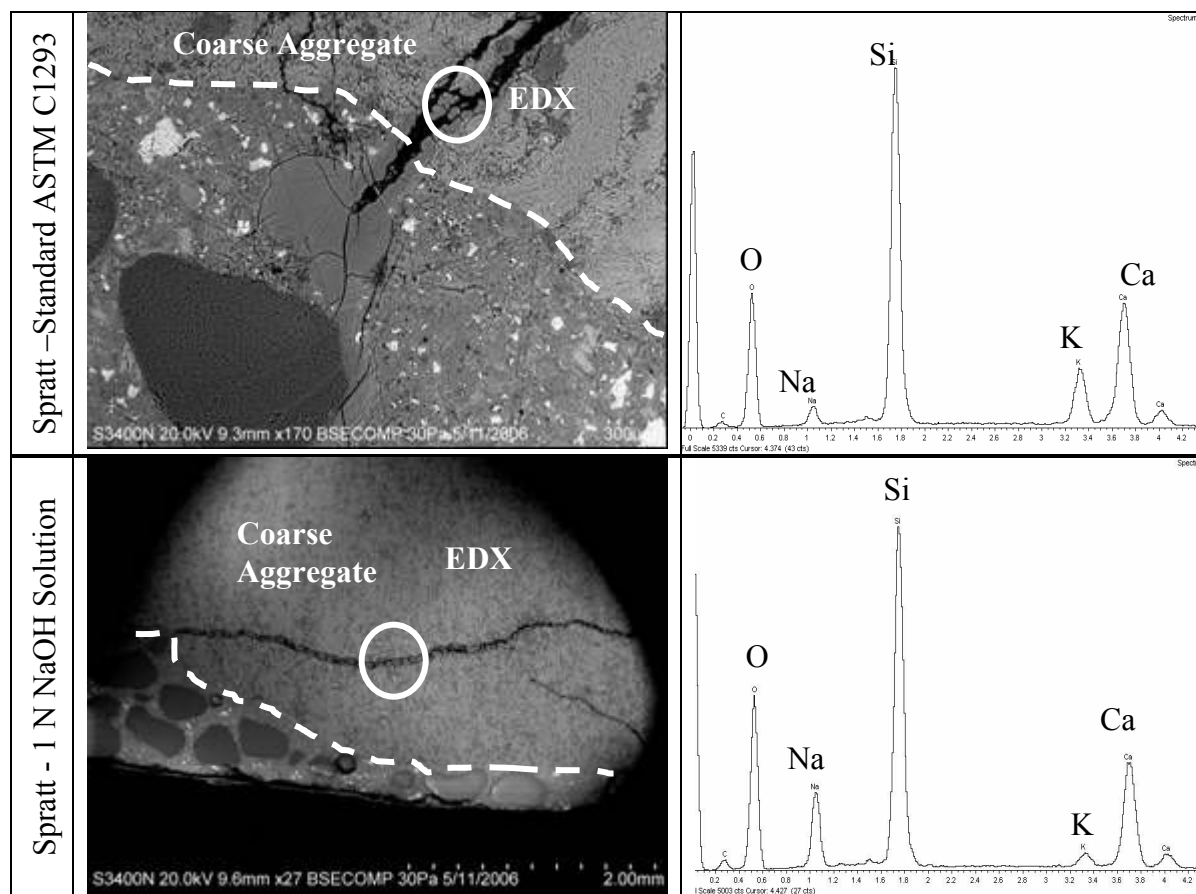


Figure 7. SEM images and EDX spectra from reacted Spratt limestone aggregate particles from prisms in standard ASTM C 1293 test or soaked in 1N NaOH solution. The white-dashed lines in these figures delineate the coarse aggregates in the SEM images.

Figure 8 shows the SEM images from polished sections of Spratt limestone concrete prisms soaked in KAc, NaAc and NaFr deicer solutions. Also, Figures 7 and 8 present the EDX spectra obtained from the ASR gel present within the reacted aggregate particles.

Based on the evidence presented in Figure 7, it is apparent that Spratt limestone is in fact highly reactive in the standard ASTM C 1293 test and in presence of 1N NaOH solution. Similar behavior is observed in the concrete in presence of KAc, NaAc and NaFr deicer solutions. In all the cases, the cracks observed in the polished section predominantly traverse through the reacted coarse aggregate particle. Typically, the ASR gel is either completely infilling the cracks in aggregate and paste or is present as a lining on the walls of the cracks in the aggregates.

The EDX spectra of reaction product present within the reacted aggregate particle (as shown in Figures 7 and 8) clearly shows the evidence of alkali-silica rich gel in each of the four soak solutions. However, the specific alkali from the soak solution appears to be the most dominant alkali present in the ASR gel in each of the cases in the modified ASTM C 1293 tests. In case of the standard ASTM C 1293 test, the alkali contributed from the cement appears to be the dominant alkali present in the ASR gel.

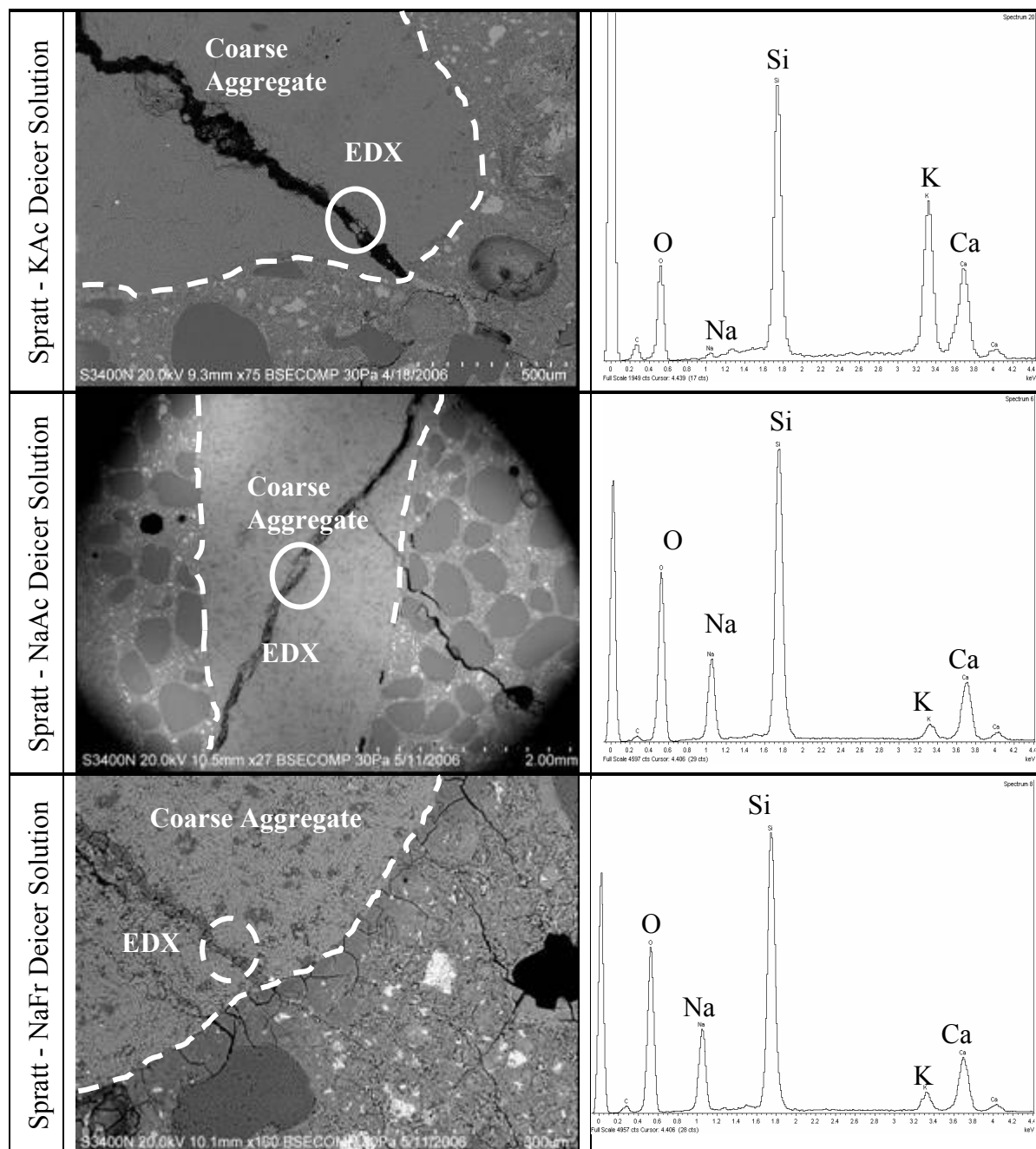


Figure 8. SEM images and EDX spectra from reacted Spratt limestone aggregate particles from prisms soaked in KAc, NaAc and NaFr deicer solutions. The white-dashed lines in these figures delineate the coarse aggregates in the SEM images.

Figure 9 shows the back-scattered SEM image of the IL dolomite concrete prism from the modified ASTM C 1293 test, prepared with LA cement and soaked in KAc deicer. Although IL dolomite is not a reactive aggregate, significant expansion was observed in prisms prepared with LA cement as shown in Figure 4b. The distress in these specimens appears to be induced by

formation of a secondary reaction product in the cement paste surrounding an aggregate particle. The EDX spectrum of the reaction product (shown in Figure 9) indicates this reaction product to be primarily a phase rich in potassium sulfate. Additional investigation is necessary to ascertain the nature of the reactions between deicer and cement paste to positively identify the source of potassium sulfate phase.

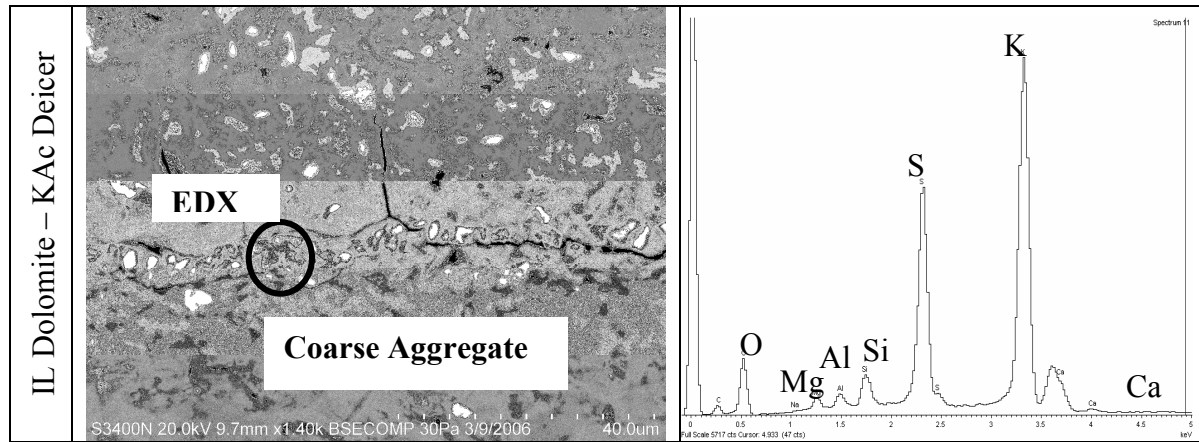


Figure 9. SEM image and EDX spectrum from IL dolomite prism soaked in KAc deicer solution.

CONCLUSIONS

Based on the observations of length-change, dynamic modulus of elasticity, microstructure of test specimens, and pH changes in the soak solutions in the standard and modified ASTM C 1260 and 1293 tests it can be concluded that:

1. KAc, NaAc and NaFr deicer solutions are capable of triggering deleterious alkali-silica reaction in mortar and concrete specimens containing reactive Spratt limestone aggregate. No deleterious ASR related effects were observed in test specimens containing non-reactive aggregates such as Ottawa sand and/or IL dolomite.
2. For prisms prepared with a cement of given alkalinity and given source of reactive aggregate, exposure to certain deicer solutions caused more distress (expansion and loss in DME) than exposure to 1N NaOH solution in the modified ASTM C 1260 and ASTM C 1293 tests. Among the three deicers evaluated in this study, the KAc deicer solution was found to be more aggressive than other deicer solutions with Spratt limestone aggregate.
3. Significant increase in pH of the deicer solutions due to interactions with hydrated cement paste in mortar bars and concrete prisms appears to be one of the primary mechanisms to trigger ASR in presence of alkali-acetate and alkali-formate deicer solutions.
4. The composition of the ASR gel observed in the concrete prisms exposed to the deicer solutions was similar to that observed in prisms exposed to 1N NaOH solution, with the specific alkali ion observed in the ASR gel being that present in the corresponding soak solution.

RECOMMENDATIONS

Further investigation is necessary to develop better understanding of the interaction between deicer solutions and calcium hydroxide in hydrated portland cement paste in order to explain the sudden and the rapid jump in pH. The fate of acetate and formate ions in these interactions need to be studied to better explain the observed behavior in test specimens. In addition, reactions leading to formation of potassium sulfate rich phases in cement paste and their effect on the integrity of the test specimens (as observed in IL dolomite prisms prepared with LA cement and soaked in KAc deicer solution) needs to be investigated.

ACKNOWLEDGEMENTS

The support of Innovative Pavement Research Foundation (IPRF) and FAA for this project is gratefully acknowledged. The author would like to thank and acknowledge the experimental work conducted by his former Ph.D. student - Dr. Ketan Sompura of Sika Corporation. The experimental data presented in this paper is part of Dr. Ketan Sompura's Ph.D. thesis at Clemson University. The author would also like to thank Profs. Jan Olek and Sidney Diamond of Purdue University for their help and guidance during the course of this research study.

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